

## PATENT SPECIFICATION

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## PROVISIONAL SPECIFICATION

## The Manufacture of New Stabilised Diazo Compounds and Compositions of Matter

We, KENNETH HERBERT SAUNDERS and MAURICE ARTHUR THOROLD ROGERS, both of Hexagon House, Blackley, Manchester both British Subjects, and IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a Company incorporated under the laws of Great Britain, do hereby declare the nature of this invention to be as follows:—

This invention relates to the manufacture of water-soluble stabilised diazo compounds by the reaction of diazo compounds derived from arylamines of the benzene or naphthalene series free from water-solubilising groups on the crude or partly purified hydrolysis products of glue, gelatine, gluten and similar proteid matter.

A further aspect of the invention is the separation of the said stabilised diazo compounds from the reaction solution by conjoint precipitation with a coupling component, thus producing a new composition of matter.

Our preferred method of procedure according to the invention is to add to the crude or partly purified solution of hydrolysed glue or other proteid matter, only a fraction of the amount of diazo compound necessary fully to exhaust the combining capacity of the said solution, that is an amount which may be conveniently equivalent to about one fifth of the total combining capacity with the diazo compound of the hydrolysed glue, but we do not confine ourselves to this ratio. By this means we avoid the formation of unutilised by-products and obtain a more suitable stabilised diazo compound. From such a solution the stabilised diazo compounds are not readily completely isolated by the normal methods of salting out and, as we have discovered, it is preferable to secure the separation of the stabilised diazo compound by the addition to the reaction liquor previous to salting out of an alkaline solution of the sodium salt of a suitable coupling component, that is one free from sulphonic or carboxylic groups, for instance, the arylamides of 2:3-hydroxynaphthoic acid and of aceto-acetic acid, beta-

naphthol, oxycarbazolcarboxylic arylides and others. There results the precipitation of a product composed jointly of what appears to be the sodium salt of the stabilised diazo compound and the coupling component.

The following examples illustrate but do not limit the invention. The parts are by weight.

## EXAMPLE 1.

100 parts of glue are hydrolysed by boiling for 24 hours with 300 parts of 25% sulphuric acid. The solution is limed, filtered from calcium sulphate and the calcium salts in solution converted to sodium salts by the addition of excess of sodium carbonate. After filtering the solution of sodium salts of the hydrolysed glue is concentrated to 350 parts and 20 parts of anhydrous sodium carbonate dissolved in the warm solution, after which it is filtered if necessary and cooled to 10–15° C. A diazo solution prepared in the usual manner from 21.3 parts of 4-chloro-2-toluidine is run into this solution of the sodium salts of hydrolysed glue during 15 minutes with stirring and cooling. It is quickly converted to the stabilised condition as shown by the rapid disappearance of the diazo reaction. 26.3 parts of 2:3-hydroxynaphthoic anilide previously dissolved in 250 parts of water and 10 parts of caustic soda (100%) is warmed to 50–60° C., run into the stabilised diazo solution and the whole then warmed to about 50° C., adding more caustic alkali if necessary to retain the 2:3-hydroxynaphthoic anilide in solution, filtered, saturated with common salt and cooled. A dark oily precipitate is thrown down which slowly sets to a gel or tar on standing. It is collected by decanting the mother liquor and dried in vacuo. The stabilised diazo compound above is in excess of the coupling component and a further quantity of hydroxy-naphthoic anilide as determined by dye or printing trials, is added until equivalent quantities of the two azo dyestuff components are present in the mixture. If desired, an approximately equivalent quantity of arylamide and stabilised diazo compound can be mixed

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previous to salting out, but we prefer to proceed in the manner above described, making subsequent adjustment as explained.

#### 5 EXAMPLE 2.

100 parts of glue are hydrolysed by heating in an autoclave for 36 hours at 140—145° C. with 400 parts of water and 20 parts of lime. The filtered product is converted to the copper salts by treatment with copper carbonate in excess, filtered and evaporated to dryness. The dry copper salts are extracted with methanol, and the methanol extract evaporated to dryness, dissolved in water and the copper removed with hydrogen sulphide. The solution is adjusted to approximately 250 parts and made alkaline with 25 parts of anhydrous sodium carbonate and cooled to 4—8° C. Into this solution is run while cooling and stirring, a diazo solution prepared in the usual manner from 21.3 parts of 5-chloro-2-toluidine, the solution being

maintained in an alkaline condition throughout the addition. The stabilised diazo compound is rapidly formed as shown by disappearance of the diazo reaction. 36 parts of the 4-bromo-2-azobenzene-2-sulphonamide of 2:3-hydroxyphenylthioic acid are dissolved in 450 parts of water and 10 parts of caustic soda (100%) and the warm solution added to the stabilised diazo compound solution, adding more caustic alkali if necessary and the whole then filtered from any tar-like precipitate and saturated while warm with salt. A thin oily precipitate is formed which becomes semi-crystalline on standing in the cold. It is collected by decantation, dried in vacuo to a brown, easily friable mass and standardised by adding more coupling component as determined by dye or printing trial, as explained in Example 1.

Dated the 28th day of June, 1935.

E. A. BINGEN.

Solicitor for the Applicants.

### COMPLETE SPECIFICATION

#### The Manufacture of New Stabilised Diazo Compounds and Compositions of Matter

We, KENNETH HERBERT SAUNDERS and MAURICE ARTHUR THOROLD ROGERS, both of Hexagon House, Blackley, Manchester, both British Subjects, and IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a Company incorporated under the laws of Great Britain, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to the manufacture of compositions suitable for use in textile printing by a process which comprises precipitation together from an aqueous alkaline solution, of an ice colour coupling component, which can be salted out from its aqueous solution and a diazoamino or diazoimino compound formed by the interaction of a diazo compound with the hydrolysis products of glue, gelatine, silk and similar proteid substances (see Plimmer, "Practical Organic and Biochemistry" (1915), p.359 et seq.).

The manufacture of water-soluble diazoimino compounds from proline (pyrrolidine- $\alpha$ -carboxylic acid) and hydroxyproline ( $\gamma$ -hydroxypyrrolidine- $\alpha$ -carboxylic acid) is described in British Specification No. 422,195. It is known (see E. Fischer and Abderhalden, Berichte der deutschen Chem. Gesell-

schaft, 1904, 37, 3072) that these cyclic imines are present together with other nitrogenous compounds in the hydrolysis products of the aforementioned proteid substances. Isolation of pure proline or hydroxyproline from a mixture of hydrolysis products is at present technically difficult because of the complexity of the operations involved.

We have now found that it is possible to make use of the mixture of compounds obtained by hydrolysing the described proteid substances, more especially that obtained by hydrolysing glue or gelatine, in the manufacture of compositions useful in textile printing. For this purpose we have devised a novel method of simultaneous precipitation.

According to the invention we add a diazo compound to an alkaline aqueous solution of an aforementioned proteid hydrolysis mixture, and then add to the solution or suspension obtained a solution of an ice colour coupling component which itself may be easily precipitated from its aqueous solution (e.g. of an arylamide of 2:3-hydroxyphenylthioic acid, 2-hydroxycarbazole-3-carboxylic acid, 7-hydroxy- $\alpha$ -naphthocarbazole-6-carboxylic acid, 2-hydroxyanthracene-3-carboxylic acid or an arylamide of acetoacetic acid), and finally we separate out and dry the desired composition. When the alkali salts of the above coupling components are precipitated in presence of the diazo-

amino or diazoimino compounds they collect these upon themselves. The mixture is thus precipitated as a homogenous semi-solid mass. It is isolated either by decantation of the liquor or by centrifuging. When dry it forms the new composition.

By applying such a composition with the aid of printing assistants to textile material in the known manner and developing in steam containing acetic acid or other volatile organic acid vapour, various fast shades may be produced.

The diazoamino or diazoimino compounds obtained as stated cannot be satisfactorily isolated in the ordinary manner, e.g. by salting out, as they either will not separate or are precipitated as a thin oil which settles slowly and incompletely owing to the dispersing effect of other substances present. But we find that these stabilised diazo compounds, whatever their nature may be, can be effectively collected in an easily handled form as above described.

In general we prefer to add an amount of coupling component less than that equivalent to the full combining capacity of stabilised diazo compound present and then, having isolated the semi-solid mass as described, we determine by dye trial the additional amount of arylamide necessary for an optimum balance of reagents. We then mix the determined quantity of dry coupling component with the mass, whereupon the whole is dried.

The determination of the requisite amount of coupling component to be added is carried out by taking a weighed quantity of the material, dissolving in water, thickening and making a print which is developed by acid steam as described in Example 1. The developed print is immersed in aqueous 1% caustic soda solution for 15 seconds, steamed in dry steam for 1 minute and immersed in a solution of a diazo compound, preferably one which will give a contrasting shade to the print. If excess coupling component is present the print is surrounded by a halo or the new colour. If no halo appears, a further weighed quantity of the material is taken, mixed with a weighed quantity of the coupling component, dissolved, printed, developed and tested as above. The process is continued until by trial and error the test shows a slight definite halo, thus indicating a small excess of coupling component.

Coupling component, not necessarily as sodium salt, is then added to the bulk of the material in the proportion indicated.

The invention is illustrated but not limited by the following examples. The 65 parts are by weight.

#### EXAMPLE 1.

250 parts of glue are hydrolysed by boiling for 24 hours with 750 parts of 25% aqueous sulphuric acid. To the solution lime is added until it is neutral, the calcium sulphate is filtered off and the calcium salts in the filtrate are converted into sodium salts by the addition of a small excess of sodium carbonate. After filtering, the solution is concentrated to 600 parts and in it are dissolved 20 parts of anhydrous sodium carbonate after which it is again filtered, if necessary, and cooled to 10°—15° C. A diazo solution prepared in the usual manner from 21.3 parts of 4-chloro-2-toluidine is run with stirring, the temperature being kept at 20° C. or lower. The diazo reaction rapidly disappears and after 15 minutes the solution is made alkaline to phenol phthalein. 19.7 parts of 2:3-hydroxynaphthoic anilide previously dissolved in 200 parts of water and 7.5 parts of sodium hydroxide is now added and the whole warmed to 50—60° C. for 15 minutes, filtered, cooled to 10° C. and common salt is added until no more will dissolve. A dark oily precipitate is thrown down which slowly sets to a gel or tar on standing. It is collected by decanting off the mother-liquor and dried in vacuo at or below 50° C. If necessary, a further quantity of 2:3-hydroxynaphthoic anilide, as determined by dye or printing trials, is added until the anilide is in a slight excess. The whole is then ground together forming a pale brown powder.

Instead of the 19.7 parts of 2:3-hydroxynaphthoic anilide, 14 parts of acetoacet-o-toluidide may be used.

#### EXAMPLE 2.

Glue is hydrolysed and the hydrolysate extracted with alcohol as described by E. Fischer and Abderhalden, *Berichte der deutschen Chem. Gesellschaft*, 1904, 37, 3072 et seq.

40 parts of the dried residue from the alcoholic extract are dissolved in 100 parts of water and 15 parts of sodium carbonate and boiled gently until all volatile amines are expelled. The solution is cooled to 10—15° C. and stirred while there is added over 15 minutes the solution obtained by diazotising 15 parts of 2:5-diethoxy-4-benzoylaminoaniline. When combination is complete the solution is made alkaline to phenol phthalein and then 7 parts of 2:3-hydroxynaphthoic anilide dissolved in 50 parts of water and 2 parts of sodium hydroxide are added and the whole warmed to 50° C., filtered after 30 minutes and cooled to 10° C. To the clear

solution is added sufficient solid caustic soda to make a 10% solution whereupon a black oil separates, which is allowed to settle, collected by decantation and dried in vacuo. It is standardised by dye trials as described in Example 1.

#### EXAMPLE 3.

Gelatine is hydrolysed and treated as described by Kingston and Schryver (Biochemical Journal, 1924, 18, 1070) and the amino acids of those carbamates soluble in alcohol-water (2:1) collected, boiled for 12 hours with 10% aqueous sulphuric acid, then made alkaline with sodium carbonate and boiled until all free amines are expelled. Sufficient of the solution is taken to provide 25 parts of the mixed amino acids formed as a result of this treatment. To this is added at 10—15° C. a solution made by diazotising 7.9 parts of 4-chloro-2-anisidine and the solution is kept alkaline by adding aqueous sodium carbonate as necessary. A brown solution is obtained. When on test it is found that free diazo compound is no longer present, the whole is made alkaline to phenol phthalein and a solution of 5 parts of 2:3-hydroxynaphthoic-*o*-anisidide dissolved in 15 parts of water and 1.5 parts of sodium hydroxide is added. The solution is warmed to 50—55° C., filtered after 15 minutes, stirred with 7 parts of green earth and 0.1 part of aluminium powder until the solution is clear golden yellow and again filtered. To the clear solution sufficient solid caustic soda to make a 15% solution is added. The precipitate which results is collected as a honey-like oil by centrifuging, dried in vacuo and standardised by dye trial as described in Example 1. Instead of 2:3-hydroxynaphthoic-*o*-anisidide, 8 parts of the *p*-chloroanilide of carbazole-2:3-hydroxy carboxylic acid may be used.

#### EXAMPLE 4.

Gelatine is hydrolysed and worked up through the copper salts of the amino acids as described by Brazier, Biochemical Journal, 1930, 24, 1188 et seq. The copper salts soluble in methyl alcohol are dissolved in water, decomposed by hydrogen sulphide, filtered and made alkaline with sodium carbonate. An amount of solution of at least 10% strength (i.e. concentrated if necessary by evaporation) containing 65 parts of the mixed amino acids is stirred at 10—15° C. while there is run in a diazo solution prepared in the usual manner from 21.3 parts of 5-chloro-2-toluidine, the solution being kept alkaline throughout the addition. The diazo compound rapidly

enters into combination. 36 parts of the 4-bromo-2-aniside of 2:3-hydroxynaphthoic acid are dissolved in 450 parts of warm water and 10 parts of sodium hydroxide and the warm solution is added to the above solution, more caustic alkali is added if necessary and the whole is filtered from any tar-like precipitate and, while still warm, an excess of common salt is added. An oily precipitate is formed which becomes semi-crystalline on standing in the cold. It is collected by decantation, dried in vacuo to a brown, easily friable mass and standardised by adding more coupling component as determined by dye or printing trial, as explained in Example 1.

Instead of the 4-bromo-2-anisidide the *o*-toluidide of 2:3-hydroxynaphthoic may be employed in the above example.

#### EXAMPLE 5.

8 parts of a composition prepared according to Example 1 using 2:3-hydroxynaphthoic anilide are dissolved in 25 parts of water at 50—70° C. containing 0.4 parts of caustic soda. This is stirred into 75 parts of starch-tragacanth thickening and the paste printed on calico. The print is dried and steamed for two minutes in steam containing the vapours of acetic acid, whereupon the parts printed become bright red. The printed material is now boiled in aqueous soap solution (5 grams per litre) for five minutes and dried. The printed areas now have a bright scarlet shade.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. Process for the manufacture of dry compositions suitable for use in textile printing which comprises adding an alkaline aqueous solution of an ice colour coupling component, capable of being precipitated from its aqueous alkaline solution, to an aqueous solution containing a compound or compounds obtained by the action of a diazo compound on a mixture of amino acids derived from the hydrolysis of a proteid substance, and salting out the mixture thus obtained, separating the precipitate and drying it.

2. Process according to Claim 1 in which the proteid substance which is hydrolysed is glue or gelatine.

3. Process for the production of compositions suitable for use in textile printing substantially as described with reference to each of the foregoing examples.

4. Compositions of matter whenever obtained by the process claimed in the

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preceding claiming clauses or its obvious chemical equivalent.

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5. A process of textile printing wherein there is used a composition as claimed in 5 Claim 4.

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